

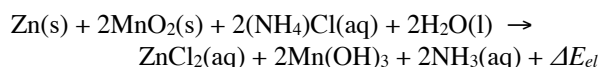
Notes from the Oesper Collections

The Leclanché Cell

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The previous three issues of *Museum Notes* have described the Edison nickel-iron alkaline storage cell (1), the Daniel gravity cell (2), and the Grove and Bunsen cells (3) respectively. This issue will deal with yet a fifth cell of historical importance found among the collection of voltaic cells donated to the Oesper Collections some years ago by the Chemistry Department of Oberlin College – the primary Leclanché cell. First described by the French scientist, Georges Leclanché, (figure 1) in 1868 (4, 5), this cell is based on the net cell reaction:



in which Zn(0) is oxidized to Zn(II) at the anode, Mn(IV) is reduced to Mn(III) at the cathode, and the resulting net cell potential is roughly 1.4 V.

Like the Edison cell described earlier, the Leclanché cell was a single-fluid system that employed a



Figure 1. A portrait medallion commemorating Georges Leclanché (1838-1882).

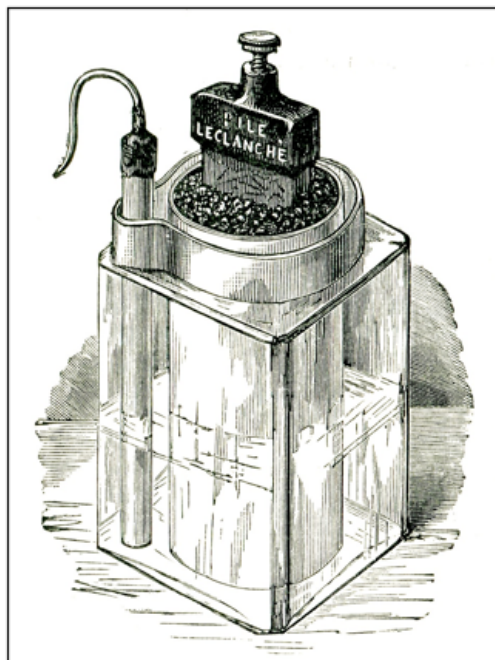


Figure 2. The Leclanché cell as depicted in Benjamin's 1893 treatise on the voltaic cell.

saturated aqueous solution of ammonium chloride [(NH₄)Cl] as the electrolyte. As originally conceived, the MnO₂(s) and an inert rectangular carbon cathode came sealed in a large porous ceramic spacer (figures 2-3) and the Zn anode as a separate rod. Both of these were placed in a large rectangular glass battery jar and the jar half-filled with the (NH₄)Cl(aq) electrolyte. To increase the conductivity of the MnO₂(s), it was intermixed with an equal quantity of powdered carbon.

Later several alternative forms of the cell were developed in which the ceramic spacer was eliminated. Rather than using loosely powdered MnO₂(s) in a ceramic cup, the MnO₂(s) and C(s) were instead mixed with a resin binder and pressed into various electrode configurations. In the form shown in figures 4-6, they were shaped into a hollow cylinder that surrounded the Zn rod used as the anode.

The Dry Cell

Starting around the last decade of the 19th century, the so-called “wet form” of the Leclanché cell was gradually transformed into the modern “dry cell” (figure 7), which is the version most commonly used today. Generally attributed to the German, Carl Gassner, around



Figure 3. An example of an early Leclanché cell similar to that in figure 2 (Jensen-Thomas Apparatus Collection).

1888, this transformation involved two major structural changes: Firstly, the Zn rod anode was replaced with a Zn can which also acted as the cell container. Sec-

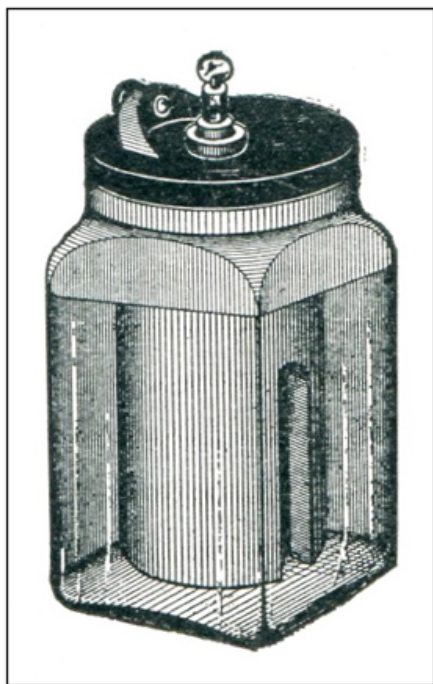


Figure 4. A circa 1909 jar form of the Leclanché cell in which the MnO₂/C cathode has been shaped into a hollow cylinder with a Zn rod anode in the center.

ondly, the MnO₂/C mixture was formed into a cylinder surrounding a central carbon rod cathode, and the space between it and the Zn can filled with a starch and flour-based electrolyte paste containing (NH₄)Cl(s) and a small amount of ZnCl₂(s). In later versions, the MnO₂/C mixture and electrode paste were mixed together and the Zn anode can furthered encased in an outer steel can and sealed at the top (figure 8) in order to help contain any leaks due to chemical corrosion of the Zn liner.

According to Vinal, these changes also altered the net cell reaction to (6):

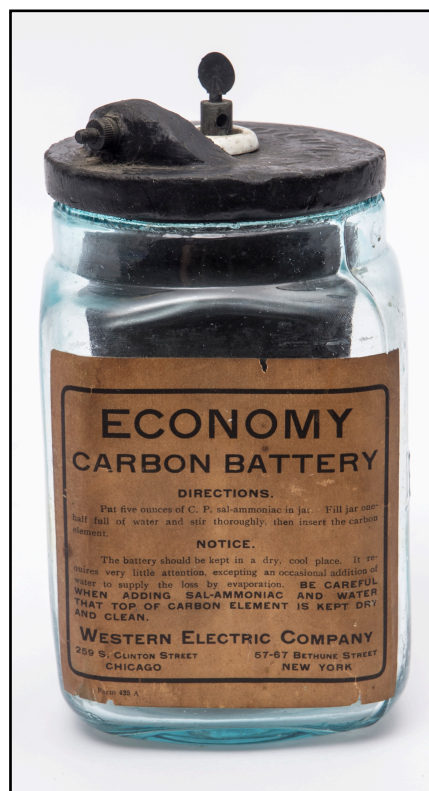
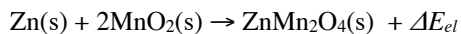


Figure 5. An actual surviving Western Electric version of the cell shown in figure 4 (Jensen-Thomas Apparatus Collections). Note the use of the inappropriate name “Economy Carbon Battery” rather than Leclanché cell.



in which Zn(0) is once again oxidized to Zn(II) at the anode, Mn(IV) to Mn(III) at the cathode, but the net cell potential is slightly increased to 1.5 V

Dry cells began to appear in laboratory supply catalogs around 1900 (7) and came in various sizes, ranging from the size D-cells still used in flashlights to the larger pint-size A cells once widely used in laboratory apparatus and by electrical hobbyists.

THE LECLANCHÉ CELL



Figure 6. The cell in figure 5 shown from the back so as to more clearly display the cylindrical MnO₂/C cathode and the central Zn rod anode.

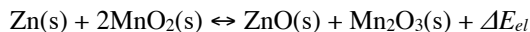
The Alkaline Cell

A second fundamental change in the Leclanché cell occurred in the late 1950s when the Canadian engineer,



Figure 7. A circa 1890 etching of two of Gassner's early dry cells. The gap between the outer Zn case and the central MnO₂/C cathode containing the electrolyte paste is clearly visible in each case.

Lewis Urry, replaced the slightly acidic (NH₄)Cl-ZnCl₂ mixture in the electrolyte paste with K(OH). Now known as the alkaline battery, this modification was finally patented by Union carbide in 1960 and is supposedly based on the net cell reaction:



in which Zn(0) is oxidized to Zn(II) at the anode, Mn(IV) is reduced to Mn(III) at the cathode, and the net cell potential remains at 1.5 V. However, it is not apparent whether this reaction is really all that different from the one given earlier by Vinal for the original (NH₄)Cl(aq) dry cell, since:

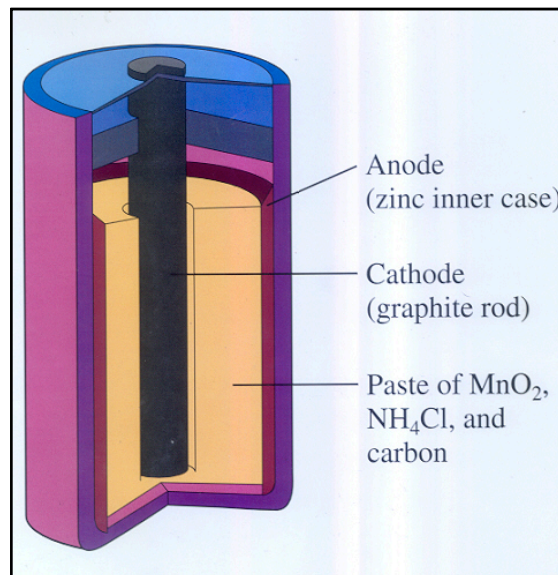
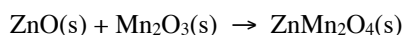
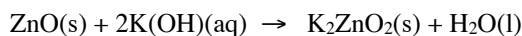


Figure 8. A cutaway diagram of a typical (NH₄)Cl/ZnCl₂ dry cell.

or why, in the presence of K(OH), the ZnO does not end up as K₂ZnO₂ instead:



To further minimize leakage due to corrosion of the Zn liner, the mechanical arrangement of the cell's contents was also reversed in the alkaline cell (figure 9). A hollow cylindrical MnO₂/C cathode was now placed next to the outer steel casing and powdered Zn and a Zn rod anode placed in the center, all of these components being intermixed with the K(OH)(aq) paste electrolyte. Your everyday AA and AAA sized cells are now all of this alkaline variety.

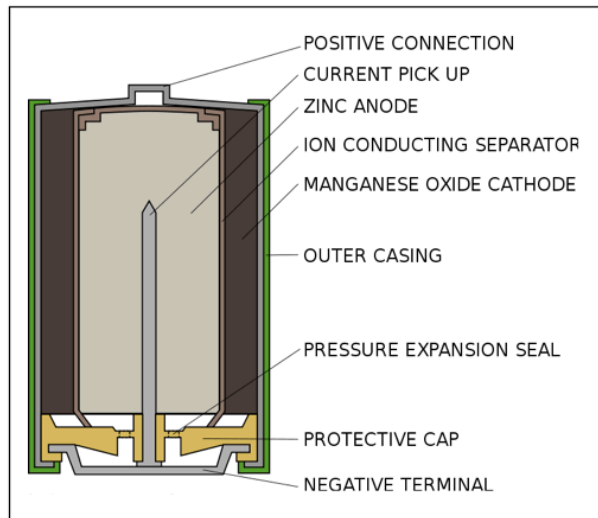


Figure 9. A cutaway diagram of a typical alkaline dry cell.

References and Notes

1. W. B. Jensen, "The Edison Nickel-Iron Alkaline Storage Cell," *Museum Notes*, July/August, 2013. Oesper Website.
2. W. B. Jensen, "The Daniell Cell," *Museum Notes*, September/October, 2013. Oesper Website.
3. W. B. Jensen, "The Grove and Bunsen Cells," *Museum Notes*, November/December, 2013. Oesper Website.
4. I have been unable to locate a detailed biographical account for Leclanché.
5. G. Leclanché, "Pile au peroxyde de manganèse à seul liquide," *Les mondes.*, **1868**, 16, 532-xxx.
6. G. W. Vinal, *Primary Batteries*, Wiley & Sons: New York, NY, 1950, pp. 32-33.
7. Thus the 1901 edition of *Catalogue of Chemical & Scientific Apparatus*, Townson & Mercer: London, 1901 lists seven brands of dry cells for sale, in as many different sizes and varieties, whereas the 1894 edition lists none.